

THERMODYNAMIC MODELING OF THE VAPOR IN EQUILIBRIUM WITH APOLLO 17 BASALTS.

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Introduction: Lunar mare basalts sampled during the Apollo 17 mission provide insight to the chemical evolution of mare basalt magmas and their associated vapor as these samples erupted and cooled rapidly at the lunar surface. We focus on minerals present on vesicle and vug surfaces in Apollo 17 basalts, such as 71036, which was opened as part of the Apollo Next Generation Sample Analysis (ANGSA) program. The mineral assemblage observed includes native Fe, SiO₂, and a Mg-P mineral, possibly merrillite [1, 2]. The petrographic context of these phases suggests that they may have been deposited directly from the vapor phase after eruption. Here we use thermodynamic modeling to assess the plausibility of the vapor-phase deposition hypothesis.

Model: We use data from high-Ti mare basalts (71035, 71037, and 71055 from the Lunar Sample Compendium [3]) as proxies for 71036, which lacks a published bulk composition, but is likely similar to these other Apollo 17 basalts which were sampled from the same boulder. This composition is modeled using the Gibbs Equilibrium Module of HSC Chemistry™ (Metso Outotec) to determine the thermodynamic equilibrium composition of the vapor as a function of temperature at 0.01 bar. Our first order goal is to determine under what conditions—if any—the vapor in equilibrium with the 71036 magma contains a significant amount of the critical constituents of the observed vapor phase minerals: Fe, Si, Na, Mg, and P.

Species were separated into phases for calculations: ilmenite, plagioclase, clinopyroxene (CPX), orthopyroxene (OPX), olivine, silica, metal, silicate and iron melts, and vapor, with solid-solution permitted where appropriate (e.g. olivine, CPX, OPX, ilmenite) assuming ideal mixing between the component species.

Gas phase species include oxides, hydroxides, chlorides, sulfides, fluorides, and pure elements. The silicate liquid was modeled as an ideal mixture of liquid oxides for all major and minor elements present in the bulk chemistry data [3], except for S and P which were added as FeS and Ca₃(PO₄)₂ liquids, respectively. Trace elements, where applicable, were added based on the average abundances of Apollo 17 samples with bulk chemistries similar to 71036.

Preliminary Results: Fig. 1 displays the stable phases as a function of temperature at 0.01 bar. Vapor dominates above ~2900 K, with some silicate melt

present. Iron liquid is stable between 1800 - 2300 K. Although this model is not designed to predict mineral-melt equilibria, minerals were included to more accurately calculate the thermodynamics of the composition at a given temperature. The liquid present in this magma likely would have evolved considerably from the bulk composition during crystallization and cooling.

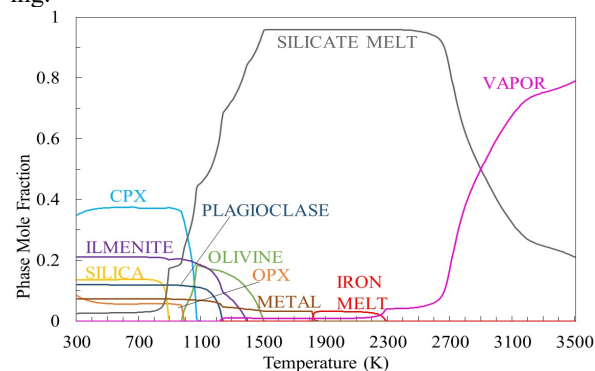


Fig. 1: Mole fraction of major phases at 0.01 bar from 300-3500 K.

Iron. The iron stability chart (Fig. 2) shows that FeTiO₃ (ilmenite) is the predominant iron phase at low temperatures, FeO in the silicate melt is favored from ~1200-2700 K, and Fe and FeO are the major iron species present in the vapor. The presence of a separate Fe liquid phase indicates that iron may have condensed into an Fe droplet before solidifying, an assertion that may be consistent with the observed morphology of 71036 Fe crystals [1, 2].

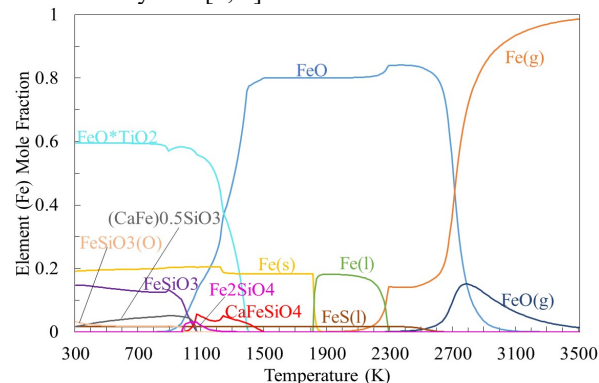


Fig. 2: Mole fraction abundance of Fe species at 0.01 bar.

Sodium. Sodium (Fig. 3) is dominated by Na in the vapor above 1200 K. Less than 5% of Na in the vapor phase is present as NaF(g).

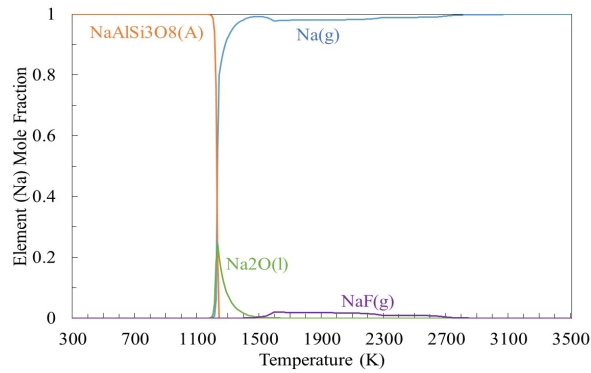


Fig. 3: Mole fraction abundance of Na species at 0.01 bar.

Magnesium. Magnesium (Fig. 4) in the vapor phase is predominantly Mg, which is present above ~2200 K, with < 10% of Mg present as MgO above 2700 K.

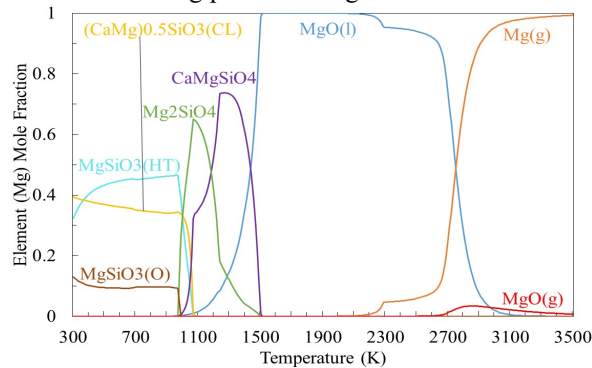


Fig. 4: Mole fraction abundance of Mg species at 0.01 bar.

Phosphorus. Figure 5 shows that phosphorus monoxide (PO) is present at ~2300 K, and is the dominate P-bearing species above 2700 K. Phosphorus dioxide (PO₂) is present between 2500-3500 K, peaking at ~2900 K where PO₂ makes up ~20% of the P. Above 3000 K, the abundance of monoatomic P(g) rises with increasing temperature, comprising ~20% of the P in the model at 3500 K.

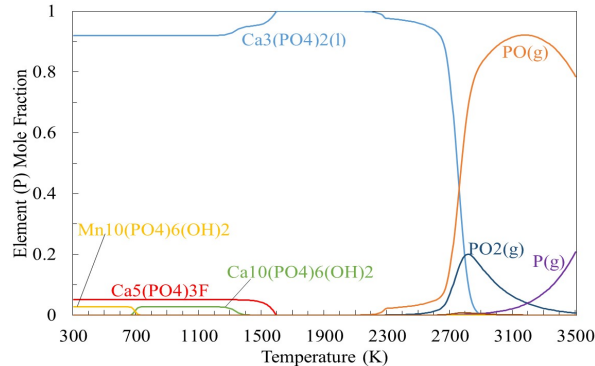


Fig. 5: Mole fraction abundance of P species at 0.01 bar.

Silicon. Figure 6 indicates that there is stable SiO in the vapor, but only above ~3000 K. This may result from an incomplete and inaccurate modeling of silica activities in solid and liquid phases, and is not considered a robust result.

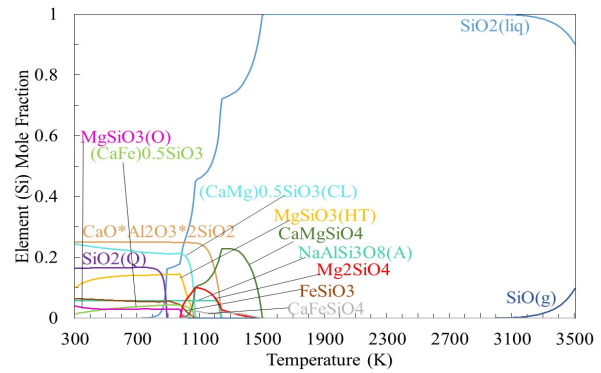


Fig. 6: Mole fraction abundance of Si species at 0.01 bar.

Discussion and Research Plan: The rapid post-eruption cooling (1-10 °C/hour [4]) of the Apollo 17 basalts that occurred on the lunar surface may have resulted in deposition of the vapor directly into crystallized minerals. However, at 0.01 bar, the temperature necessary for a vapor that carries a significant fraction of the elements required for the formation of the observed minerals is in some cases significantly higher than the presumed eruption temperatures for Apollo 17 basalts (~1700 K [5]). The formation of SiO₂ requires the highest temperatures at >3000 K, however Na minerals require the lowest at >1200 K.

Several factors influence the accuracy of the presented model. For example, all possible thermodynamically stable species of relevance must be manually included. The current model does not account for any non-ideality of species in terms of fractional vaporization or activity models, however future models will include more complex analyses to account for this. Very small fractions of species could become more significant when scavenged from a large volume, however this initial model focuses only on the more abundant species. The equilibrium has only been calculated at 0.01 bar, but pressure is likely to influence the species that are stable at different temperatures, and will be evaluated with additional calculations.

References: [1] Barnes J. J. et al. (2022) *Apollo 17-ANGSA Workshop 2022*, Abstract #2051. [2] Wilbur Z. E. et al. (2022) *Apollo 17-ANGSA Workshop 2022*, Abstract #2026. [3] Meyer C. (2007) *Lunar Sample Compendium*. [4] Donohue P. and Neal C. (2015) *Geochimica et Cosmochimica Acta*. [5] Renggli C. J. et al. (2017) *Geochimica et Cosmochimica Acta*.